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(21) International Application Number: PCT/IT97/00300 (22) International Filing Date: 5 December 1997 (05.12.97) (30) Priority Data: RM96A000849 9 December 1996 (09.12.96) IT (71) Applicant (for all designated States except US): CENTRO SVILUPPO MATERIALI S.P.A. [IT/IT]; Via di Castel Romano, 100-102, I-00129 Roma (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): MANCIA, Franco [IT/IT]; Via dei Ciclamini, 106, I-00171 Roma (IT). FORTUNATI, Sandro [IT/IT]; Viale Giannelli, 49, I-05100 Terni (IT). NOVARO, Ezio [IT/IT]; Circonvallazione Clodia, 169, I-00195 Roma (IT). (74) Agents: IACOBELLI, Daniele et al.; Società Italiana Brevetti S.p.A., Piazza di Pietra, 39, I-00186 Roma (IT).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR PICKLING PRODUCTS IN A METAL ALLOY CONTAINING IRON AND IN TITANIUM AND ALLOYS THEREOF (57) Abstract A method for pickling products made of metal alloys containing iron, and products made of titanium and alloys thereof, in the absence of nitric acid as an oxidising agent, characterised by the fact that the product to be pickled is submerged in the anolyte (as the pickling solution) of an electrolytic cell in which the anolyte is made up of an aqueous solution of sulphuric acid, of hydrofluoric acid and optionally of phosphoric acid and hydrochloric acid, and with the catholyte made up of an aqueous solution of sulphuric acid and the oxidising agent in the pickling solution being the ferric ion, or the ions titanium(III) and titanium(IV).		

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METHOD FOR PICKLING PRODUCTS IN A METAL ALLOY CONTAINING
IRON AND IN TITANIUM AND ALLOYS THEREOF

DESCRIPTION

5 The present invention relates to a method for pickling products made of a metal alloy containing iron and, more specifically, to a pickling process for stainless steels characterised in that it avoids the use of nitric acid as an oxidising agent.

10 The present invention can also be applied for pickling of titanium and alloys thereof.

It is known that pickling is the process used to remove the layer of oxidation that forms as a result of heat treating of steel.

15 In order to achieve an effective pickling process for stainless steels and titanium, a mixture of nitric acid (HNO_3) and hydrofluoric acid (HF) is normally used, at a temperature that generally varies between 60 and 75°C.

20 However, the use of nitric acid causes serious environmental control problems, which result from the following:

- a considerable presence in the vapours over the pickling bath of nitrogen oxides (NO_x), which are developed by the pickling bath itself;
- 25 - the formation of exhausted solutions which generate nitrate-rich sludge to be disposed of;
- the high cost of disposal for waste products containing nitrates.

30 To overcome the above difficulties, a number of different methods have been drawn up in which reduction or elimination of the use of nitric acid in chemical pickling processes has been foreseen, and which are based on the use of a number of oxidants, added to the bath as reactive agents, among which, for example, it is possible
35 to include permanganates, persulphates, ferric chloride, hydrogen peroxide (H_2O_2), or mixtures thereof. In the pickling bath hydrofluoric acid is always used, in

combination with various mineral acids (generally mixtures of acids), among which: sulphuric acid, hydrochloric acid, phosphoric acid.

5 In particular, a method exists that foresees a reduction in the amount of nitrogen oxides NO_x that are developed by the bath. Said method is generally based on the use of hydrogen peroxide, which not only makes it possible, if necessary, to reduce the total amount of nitric acid in the bath and required for the process, but
10 also to oxidise the nitrogen oxides to the highest state of oxidation.

However, this method has the disadvantage that it only partially solves the problems mentioned above, as it only allows a reduction of the NO_x content in the
15 vapours, not its elimination, and it leaves the problem of nitrates in the exhausted baths unsolved. For these only partial improvements, more or less complex variations in the basic pickling process (that is to say HF/HNO_3 mixtures) are necessary.

20 Another method is known, the purpose of which is to eliminate the presence of nitric acid altogether, using sulphuric acid, ferric sulphate and hydrogen peroxide alongside the hydrofluoric acid, the presence of which remains practically unchanged in the processes examined
25 here.

However, the above method also shows the following problems:

a) complex management, deriving from the complexity of the analytical control of hydrogen peroxide in the
30 baths (this reagent is in fact unstable);

b) difficulty in maintaining the dissolution kinetics (these are strongly dependent on the redox potential of the vehicle) within the necessary values; and

35 high running costs, also deriving from the high cost of the reagents, in particular stabilised hydrogen peroxide solution.

The aim of the present invention is therefore to solve the above mentioned problems, providing a method for pickling products made of metal alloys containing iron, and products made of titanium and alloys thereof, in the absence of nitric acid as an oxidising agent, characterised by the fact that the product to be pickled is submerged in the anolyte (as the pickling solution) of an electrolytic cell in which the anolyte is made up of an aqueous solution of sulphuric acid, of hydrofluoric acid and optionally of phosphoric acid and hydrochloric acid, and with the catholyte made up of an aqueous solution of sulphuric acid, the oxidising agent in the pickling solution being the ferric ion, or the ions titanium(III) and titanium(IV), formed in the anode by oxidation of the ferrous ion, or of the ion titanium(II), resulting from dissolution of the surface layers of the product to be pickled.

According to another aspect of the invention, the catholyte of the cell is preferably made up of an aqueous solution of sulphuric acid and is sent out of the cathodic compartment into the pickling solution, to reintegrate the H_2SO_4 that is consumed during the pickling reaction.

According to the invention, the pickling bath forms the anolyte of the cell, and is maintained at a temperature preferably comprised between 45 and 85°C, and it is made up of an aqueous solution of sulphuric acid, of hydrofluoric acid and optionally of hydrochloric and phosphoric acid, with the following composition expressed as a percentage by weight:

- free HCl between 0 and 50 g/l
- free H_3PO_4 between 0 and 200 g/l
- free H_2SO_4 from 50 to 250 g/l
- free HF from 5 to 50 g/l
- Fe_{tot} in solution ≥ 50 g/l

Furthermore, the products containing iron for which the method according to the present invention is

applicable are selected from the group comprising:

- Stainless, laminated or in any case hot and/or cold worked steel, in particular austenitic, ferritic, duplex and super-stainless steel;

5 - Ni-based super-alloys.

Furthermore, the products containing titanium for which the method according to the present invention is applicable are selected from the group comprising:

10 - CP (commercial purity) Titanium of various grades;

- Titanium alloys.

The present invention will be more clearly illustrated in the following detailed description of a preferred embodiment thereof, given merely as a non-limiting example, with reference to the enclosed figures, in which:

figure 1 shows a diagram of an embodiment of the pickling bath according to the present invention; and

15 figure 2 shows a diagram of the variation in weight of the metal product according to the concentration of acids and iron ions in the pickling bath according to the present invention.

The method object of the present invention is based on the replacement of nitric acid and on the theory that this acid performs two basic operations:

25 a) it increases the total acidity of the bath; and
 b) it raises the redox potential of the vehicle, according to the oxidising properties of said acid.

The overall action of the nitric acid can thus be obtained using various reagents capable of guaranteeing these two specific actions, even separately. The reagents selected to control the total acidity are therefore mineral acids and oxidising agents.

30 Finally, as regards the use of oxidising agents, the method according to the present invention does not resort to direct addition of reagents into the bath, but uses electro-chemical treatment of the solution which

generates the desired oxidising agent directly in the pickling bath.

Specifically, the method object of the present invention is based on the use of a pickling bath that does not contain nitric acid, but contains in its place a mineral acid (for example sulphuric acid) and as an oxidant contains only the ferric ion Fe^{3+} (or, in the case of titanium, the ions Ti^{3+} and Ti^{4+}). The ferric ion is not added in the form of a reagent, but is obtained directly in the pickling solution by anodic oxidation in an electrolytic cell of the ions Fe^{2+} that are generated during the pickling process itself (dissolution of the steel). In the case of titanium, anodic oxidation of the Ti^{2+} ions to Ti^{3+} and Ti^{4+} ions is carried out in the cell.

A diagram of a preferred embodiment of the method according to the invention is illustrated in figure 1. According to the method of the invention, an electrochemical cell of the membrane type is used, worked by controlling the anodic potential or using a galvanostatic control. The cell anolyte (in which the reaction generating Fe^{3+} ions takes place) is made of the same solution as the pickling bath, whereas the catholyte used is a solution of sulphuric acid that is destined to be sent to the pickling bath.

The mineral acids used as anolyte are mixtures of hydrofluoric, sulphuric, hydrochloric and phosphoric acid.

According to the invention, the method provides a self-balancing system, that is to say one that is capable of controlling the process kinetics and the final quality of the product. The pickling kinetics are in fact directly controllable according to the speed of production of Fe^{3+} ions in the cell.

Control of the concentration of Fe^{3+} ions in the pickling bath (which can be done easily by setting the cell working parameters) also allows close control of the most critical process parameter (that is to say the redox

potential value of the system), also giving obvious advantages for the final quality of the product.

5 The use of anodic oxidation in a cell to generate the oxidant results in a considerable saving in working costs, due to the higher cost of the oxidising reagents added to the bath according to normal methods.

10 Finally, the choice of the Fe^{3+} ion as an oxidant does not involve stability problems in the bath, as is the case in certain reagents (in particular hydrogen peroxide solution requires the use of expensive stabilising agents).

15 The principles that have resulted in definition of the solutions used to apply the method according to the present invention are based on the following considerations:

a) Pickling (both using traditional processes in HF/HNO_3 solutions and using H_2O_2 -based processes) must necessarily involve the presence of an oxidant that keeps the redox potential at the necessary levels;

20 b) The presence of oxidants involves the passage of ferrous ions from Fe^{2+} (produced during the pickling reaction) to Fe^{3+} (or of Ti^{2+} to Ti^{3+} and Ti^{4+});

25 c) The ferric ions Fe^{3+} are notoriously oxidant with respect to the steel to be pickled (in fact, according to the reversible electro-chemical potentials scale it can be seen that: $E_{\text{rev}} = -447$ mV SHE for the pair Fe/Fe^{2+} ; $E_{\text{rev}} = +771$ mV SHE for the pair $\text{Fe}^{2+}/\text{Fe}^{3+}$); in a similar way the high valence titanium ions (Ti^{3+} and Ti^{4+}) are oxidant with respect to the titanium to be pickled, as we have
30 $E_{\text{rev}} = -1630$ mV SHE for the pair Ti/Ti^{2+} , whereas we have $E_{\text{rev}} = -502$ mV SHE and $E_{\text{rev}} = -368$ mV SHE for the pairs $\text{Ti}^{4+}/\text{Ti}^{3+}$ and $\text{Ti}^{3+}/\text{Ti}^{2+}$, respectively;

35 d) From the above points a), b) and c) it can be seen that there is the possibility of using the types Fe^{3+} (of Ti^{4+} and Ti^{3+}) directly as an oxidising reagent in the solution, instead of nitric acid or hydrogen peroxide;

e) The total acidity of the solution, in the absence of nitric acid, can be raised using lower cost mineral acids, such as H_2SO_4 , HCl and H_3PO_4 , either alone or in combination (see points f and g);

5 f) The hydrochloric acid performs in part the functions of the hydrofluoric acid (it is a strong de-passivating, or activating agent), but at a lower cost.

10 g) The total acidity cannot be re-established with hydrochloric acid alone, as the ion Cl^- would be too aggressive on the surface of the steel, preventing, or complicating unnecessarily, the normal final passivation treatment; the choice of a balanced mixture of the two acids HCl and H_2SO_4 helps to improve control of the electro-chemical working potentials and the dissolution
15 kinetics; when the bath is not required to be excessively aggressive it is possible to use a progressively lower concentration of HCl , even reducing the content to zero, with HF and H_2SO_4 , or alternatively mixtures of HF , H_2SO_4 and H_3PO_4 ; phosphoric acid acts using a mechanism similar
20 to that of sulphuric acid.

On the basis of the above and according to the method of the present invention, the pickling bath can conveniently use the following reagents:

25 - acids: HF and mixtures of $\text{HCl}/\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ at variable concentrations, including mixtures with HCl and/or H_3PO_4 at concentration zero;

- oxidants: ferric ion Fe^{3+} (alternatively, for titanium, Ti^{4+} and Ti^{3+}).

30 In view of the particular oxidant chosen (Fe^{3+} and/or Ti^{3+} and Ti^{4+}), the method object of the invention foresees electro-chemical treatment of the solution, by which it is possible to obtain direct formation of the oxidising agent and control of the correct concentration levels directly within the bath.

35 The principles and criteria used to prepare an electro-chemical cell that can be used to apply the method of the present invention will now be defined with

reference to figure 1. For the sake of simplicity, reference will be made to a pickling cell for metal alloys containing iron, as treatment of titanium is the same.

5 a) Anolyte

The same pickling solution is used, and is continuously circulated (but discontinuous treatment can also be foreseen) from the bath by pumping;

b) Anodic reaction: $\text{Fe}^{2+} \Rightarrow \text{Fe}^{3+}$

10 This reaction produces the Fe^{3+} that serves to maintain the concentration of the oxidising agent Fe^{3+} in the pickling bath constant. The pickling mechanism in the presence of Fe^{3+} as an oxidant takes place using the following reactions:

15 (1) $\text{Fe} \Rightarrow \text{Fe}^{2+} + 2e$ (primary oxidation semi-reaction to dissolve the metallic iron);

(2) $\text{Fe}^{3+} + e \Rightarrow \text{Fe}^{2+}$ (reduction semi-reaction).

The resulting reaction (in the bath), that is to say the sum of the two semi-reactions (1)+(2) is:

20 (3) $\text{Fe} + 2 \text{Fe}^{3+} \Rightarrow 3 \text{Fe}^{2+}$

From the reaction (3) it is found that the quantity of Fe^{3+} ions that must be generated in the cell over a period of time is equivalent to double the quantity of iron that is in solution during pickling.

25 is carried out:

(4) $\text{Fe}^{2+} \Rightarrow \text{Fe}^{3+} + e$

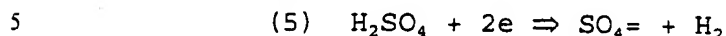
It should be noted that reaction (4) is the inverse reaction to (2). The ion Fe^{3+} reduces to Fe^{2+} during (2) in the bath and oxidises again in the cell from Fe^{2+} in (4). The oxidising capacity of the system is thus guaranteed by passage of the anodic current in the cell in reaction (4), in which the ion Fe^{3+} is a go-between and, according to the present method, no other reagents are added as oxidants.

35 c) Cathodic reaction

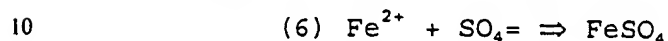
For the reaction in the cathodic part of the cell it has been found that the most practical solution is that

of using a solution of sulphuric acid as a catholyte, because of the fact that the pickling process in reference foresees the use of sulphuric acid in the bath.

The cathode reaction is therefore the following:



The catholyte is sent into the bath in an hourly amount equal to the sulphuric ion content necessary to combine with the ion Fe^{2+} generated by reaction (1), according to the following reaction:

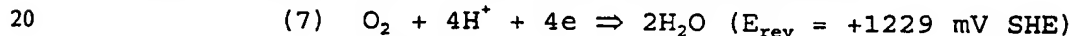


d) Anodic control

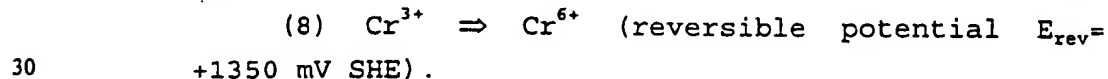
As regards control of the passage of current in the electrolytic cell, two alternatives are possible:

d.1) Potentiostatic control

15 This is performed with a minimum electrode potential of ≥ 771 mV SHE which allows the oxidation reaction (4). As regards the maximum value it is preferable to select a value that in particular does not allow development of oxygen, according to the following reaction:



The co-presence of reaction (7) and (4) would, in fact, decrease the efficiency of the cell, attenuating the undesired water hydrolysis reaction by developing oxygen. The chosen potential E is thus in the range of
25 between 771 and 1229 mV SHE. For potential values of this kind, among other things, there is no formation of chrome with valence 6 (often toxic), according to the simplified reaction:



In practice it can be of use to position at values even relatively higher than 1229 mV, taking advantage of the fact that the oxygen development reaction takes place with a certain level of overvoltage.

35 d.2) Galvanostatic control

This control is more simple and more economical to perform in the system, but the advantages indicated in

point (d.1) above might be lost, in particular there is a risk of excessive oxygen development. However, exact experimental knowledge of the characteristics of the cell and suitable control of the current make it possible to obtain the desired electro-chemical potential in the anode, also using galvanostatic control.

e) Membrane

As the anolyte and catholyte solutions are different and, in particular, in order not to decrease the efficiency of the cell, it is undesirable that there be any transmigration into the catholyte of ferric ions Fe^{3+} forming in the anolyte, the cell is provided with a suitable membrane. It is possible to use membranes of different effectiveness, working temperature and duration.

The electro-chemical cell in reference when tested in the system has provided the following performance levels, which are given below in the form of an example:

- efficiency under current: $> 90\%$
- cell potential (ΔV at terminals) $\cong 3V$
- specific power $\cong 6W/dm^2$
- anode current density $\cong 2A/dm^2$
- consumption per mole Fe^{3+} produced $\cong 0.081 \text{ kWh}$

To the above must be added that the value of the current, when the cell characteristics are known, directly expresses the Fe^{3+} ion formation speed, as per reaction (4). This makes it possible to maintain its concentration in the bath constant, when the characteristic speed of the pickling process is known.

The system thus results self-balanced, in fact the dissolution reaction (1), that is to say the pickling reaction, cannot proceed at a kinetic level superior to the cell reaction (4), as there would be a deficit in the transfer of electrons for the anodic pickling semi-reaction itself. In a similar manner, if dissolution in (5) decreases its kinetics for any reason, there would be a progressive rise in the concentration of Fe^{3+} ions in

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the bath (as the supply from reaction (4) is constant), with a corresponding rise in the redox potential of the solution and thus of the overall pickling kinetics.

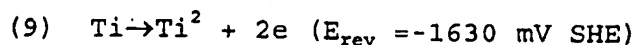
With reference to figure 1, it is shown how the dissolution kinetics of AISI 409 LI stainless steel increase as the Fe^{3+} content increases.

Finally, the proposed pickling method follows the speed of reaction (4), which can be controlled easily using the cell parameters.

As regards more specifically application of the method according to the present invention for pickling of titanium and alloys thereof, the following must be specified:

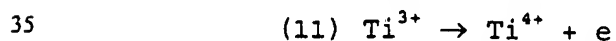
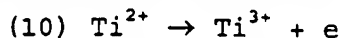
- Titanium is susceptible to pickling in the same conditions as stainless steel, that is to say traditional baths in HNO_3/HF solutions or in baths of the type without nitric acid (generally speaking, because of the higher reactivity of this element, low concentrations and temperatures of around 40-50°C are used);

- Pickling of titanium and alloys thereof shows kinetics and elementary pickling reactions that are entirely the same as regards the electro-chemical cell and method described above. In particular, it is sufficient to bear in mind that in the case of titanium the basic pickling reaction is:



The role played by the ion Fe^{3+} in reaction (2) can be substituted, if iron is not available or not desired in the bath, by the ions Ti^{3+} and Ti^{4+} , given that for the pair $\text{Ti}^{3+}/\text{Ti}^{2+}$ $E_{\text{rev}} = 502 \text{ mV}$ and for the pair $\text{Ti}^{4+}/\text{Ti}^{3+}$ $E_{\text{rev}} = -368 \text{ mV SHE}$.

In the electro-chemical cell, in this case, the following oxidation reactions take place:



The anodic cell potential in this case is selected within the range of between -368 mV SHE (oxidation of

Ti²⁺ to Ti⁴⁺) and 1229 mV SHE (development of oxygen).

The method according to a second embodiment of the invention foresees, for pickling of titanium and alloys thereof, the use of the same baths and acid solutions containing Fe³⁺ that are used for pickling of stainless steel. This method is very convenient, because the majority of titanium coil manufacturers process these coils on the same lines used for stainless steel.

In this case, in the baths containing solutions of H₂SO₄ (or other mineral acids), HF and iron ions, the titanium is pickled according to the reaction (9) (oxidation reaction), as the oxidising agent is the ion Fe³⁺, which reduces according to reaction (2), whereas in the electro-chemical cell the concentration of Fe³⁺ is restored by means of reaction (4).

Finally, as seen above, the ion Fe³⁺ (and the ion Fe²⁺ from which it is formed) does not participate in the overall reaction balance, so there is no consumption of the quantity of iron ions contained in the bath, whereas the oxidising capacity, in terms of electron transfer, is ensured by the passage of current to the cell anode.

An example of a pickling process carried out according to the method of the present invention will now be given.

EXAMPLE

The example of a pickling process refers to a coil of hot laminated and peened AISI 304 steel.

The initial pickling solution is made up of:

Free H₂SO₄ = 150 g/l

Free HF = 30 g/l

Total Fe in solution ≥ 50 g/l.

Initially the solution is made to circulate in the electrolytic cell until reaching the optimum Fe³⁺ value, equivalent to ≥ 30 g/l, and a temperature of approximately 65°C.

After this the pickling process commences (tape sent into the pickling bath) at the line speed foreseen. The

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line speed, the thickness and the width of the treated tape obviously define the production level per hour, expressed in t/h of pickled tape (e.g. at a speed of 18 metres/minute, tape thickness 3.2 mm and width 1500 mm the production of pickled tape will be approximately 40 t/h). According to the example, the tape is 3.2 mm thick (typical average thickness of hot-laminated products).

Pickling was carried out continuously in the following conditions:

- Circulation of the pickling solution in the electro-chemical cell with a production of Fe^{3+} ions ≥ 48 moles/t of pickled tape;

- Consumption (and therefore reintegration) of acids:

$\text{H}_2\text{SO}_4 \geq 1.8$ Kg/t of pickled tape;

$\text{HF} \geq 1.4$ Kg/t of pickled tape.

It will be obvious to those expert in the field that other embodiments differing from the one described above with reference to figure 1 are possible. In particular the pickling bath can be made up of the anodic part of the cell, without the need to create external circulation of the anolyte between the bath and the cell. Furthermore, as regards the catholyte, it is not necessarily essential to resort to solutions using sulphuric acid, as different electrolytes can be chosen (e.g. HCl, mixtures of HCl/ H_2SO_4 or others), including the pickling solution itself which is eliminated as waste. Input of the catholyte into the bath may also not be necessary, in particular when electrolytes other than those used in the pickling bath are chosen. All the above variations are alternatives to the one described and illustrated as the preferred embodiment, and are understood to fall within the scope of the present invention.

CLAIMS

1. A method for pickling products made of metal alloys containing iron, and products made of titanium and alloys thereof, in the absence of nitric acid as an oxidising agent, characterised by the fact that the product to be pickled is submerged in the anolyte (as the pickling solution) of an electrolytic cell in which the anolyte is made up of an aqueous solution of sulphuric acid, of hydrofluoric acid and optionally of phosphoric acid and hydrochloric acid, and with the catholyte made up of an aqueous solution of sulphuric acid, the oxidising agent in the pickling solution being the ferric ion, or the ions titanium (III) and titanium (IV), formed in the anode by oxidation of the ferrous ion, or of the ion titanium (II), resulting from dissolution of the surface layers of the product to be pickled.

2. A method for pickling products made of metal alloys containing iron according to claim 1, in which the working electro-chemical potential of the cell anode is between 771 and 1229 mV SHE.

3. A method for pickling products made of titanium and alloys thereof according to claim 1, in which the working electro-chemical potential of the cell anode is between -368 and 1229 mV SHE.

4. A method for pickling products made of metal alloys containing iron, and products made of titanium and alloys thereof according to claims 1, 2 and 3, in which the anodic reaction is potentiostatically or galvanostatically controlled.

5. A method for pickling products made of metal alloys containing iron, and products made of titanium and alloys thereof according to any one of the preceding claims, in which the pickling operations are carried out in a continuous or discontinuous manner by means of continuous or discontinuous circulation of the anolyte.

6. A method for pickling products made of metal alloys containing iron, and products made of titanium and

alloys thereof according to the preceding claim, in which the pickling bath containing the anolyte forms the anodic compartment in the electro-chemical cell.

5 7. A method for pickling products made of metal alloys containing iron, and products made of titanium and alloys thereof according to any one of the preceding claims, in which the catholyte of the electrolytic cell is made up of a solution of sulphuric acid and is sent, on leaving the cathodic compartment, into the pickling
10 solution as an anolyte.

8. A method according to the preceding claim, in which the catholyte solution is made up of any electrolyte which can either be sent into the anolyte or not.

15 9. A method according to any one of the preceding claims, in which the catholyte is made up of pickling solution and is subsequently discharged from the cathodic area as waste material.

20 10. A method for pickling products made of metal alloys containing iron, and products made of titanium and alloys thereof according to any one of the preceding claims, in which the pickling bath has a temperature of between 40 and 90°C and is made up of an aqueous solution containing the following components:

- 25
- free HCl between 0 and 50 g/l
 - free H_3PO_4 between 0 and 200 g/l
 - free H_2SO_4 from 50 to 250 g/l
 - free HF from 5 to 50 g/l
 - Fe_{tot} in solution ≥ 50 g/l

30 and alternatively, for products in titanium and alloys thereof, Ti_{tot} in solution ≥ 50 g/l.

11. A method for pickling products made of metal alloys containing iron according to any one of claims 1, 2 and 4-10, in which said products made of metal alloy
35 containing iron are chosen from the group comprising:

- Stainless, laminated or in any case hot and/or cold worked steel, in particular austenitic, ferritic,

- 16 -

duplex and super-stainless steel; and

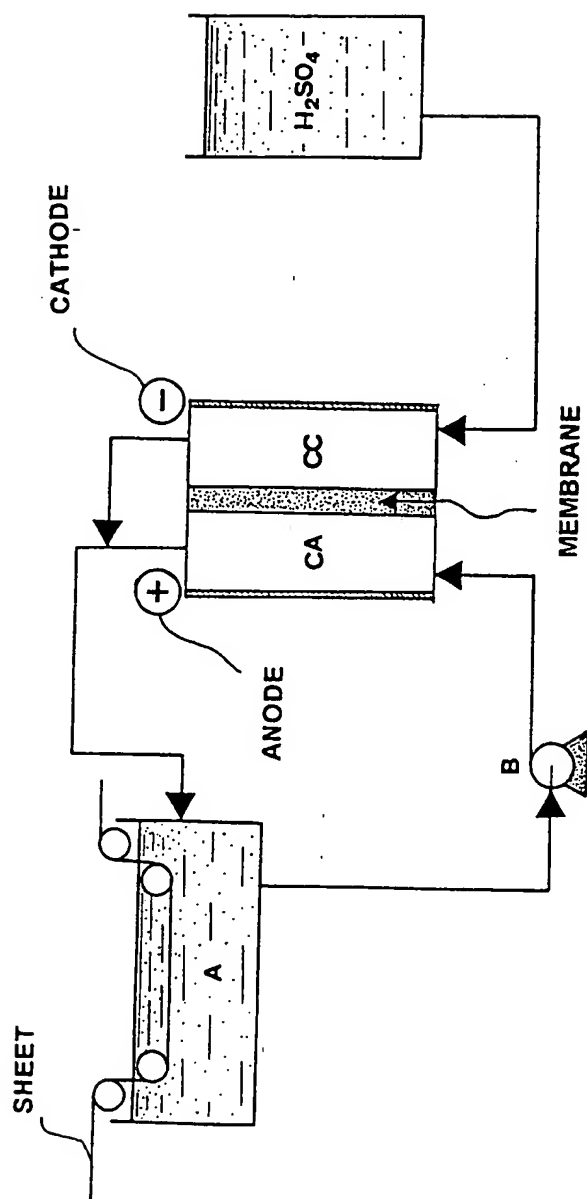
- Ni-based super-alloys.

5 12. A method for pickling products made of titanium and alloys thereof according to any one of claims 1, 3 and 4-10, in which said products containing titanium and alloys thereof are selected from the group comprising:

- CP (commercial purity) Titanium of various grades;
- Titanium alloys.

10 13. A method for pickling products made of metal alloys containing iron, and made of titanium and alloys thereof as described, exemplified and claimed above.

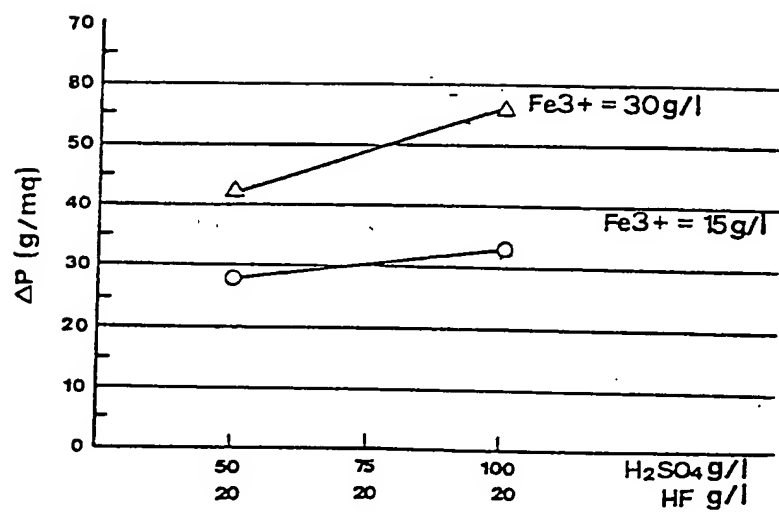
- 1/2 -



A : Pickling bath
B: Pump
CA: Anodic compartment
CC: Cathodic compartment

FIG 1

- 2/2 -



Temperature $T = 45^{\circ}C$
Time $t = 60\ s$
Material : AISI 409 LI

FIG 2

INTERNATIONAL SEARCH REPORT

In tional Application
PCT/IT 97/00300

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23G1/26 C23G1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 43463 A (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN) 20 November 1997 see whole document	1, 4-6, 8-11, 13
X	--- CHEMICAL ABSTRACTS, vol. 84, no. 20, 17 May 1976 Columbus, Ohio, US; abstract no. 139369e, ISARAI R.: "pickling of austenitic stainless steel" page 256; XP002024602 see abstract & JP 50 133 125 A (DAIDO STEEL) 22 October 1975 --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

5 March 1998

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Int'l. Patent Application
PCT/IT 97/00300

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 39 37 438 A (KRUPP STAHL AG) 30 August 1990 see column 3; claim 1 ----	1
A	EP 0 415 807 A (USINE ACIERS DE CHATILLON ET GUEUGNON) 6 March 1991 see column 5 - column 6; claims 1-12 ----	1,3,10
A	EP 0 517 234 A (NIPPON PAINT CO. LTD.) 9 December 1992 see page 6 - page 7; claims 1-9 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application

PCT/IT 97/00300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9743463 A	20-11-97	IT MI960936 A	10-11-97
DE 3937438 A	30-08-90	NONE	
EP 415807 A	06-03-91	FR 2650303 A	01-02-91
		AT 113080 T	15-11-94
		AU 634277 B	18-02-93
		AU 6168490 A	11-03-91
		CA 2037893 A	27-01-91
		DE 69013447 D	24-11-94
		DE 69013447 T	23-02-95
		ES 2064686 T	01-02-95
		FI 93371 B	15-12-94
		WO 9102109 A	21-02-91
		JP 4501139 T	27-02-92
		US 5338367 A	16-08-94
EP 517234 A	09-12-92	JP 4362183 A	15-12-92
		CA 2070484 A,C	08-12-92
		DE 69217726 D	10-04-97
		DE 69217726 T	14-08-97
		US 5248399 A	28-09-93

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